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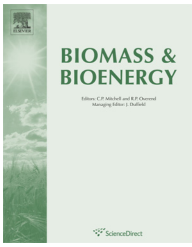

Screening of various low-grade biomass materials for low temperature gasification: Method development and application

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ABSTRACT

This work aims at identifying potential low-grade biomass fuels for a near future Danish CHP system encompassing pretreatment of these fuels by Pyroneer gasification for subsequent conversion of the gas in existing coal-fired boilers. The focus of the work is on development of a suitable screening method and the subsequent use of the method to identify promising – but currently unproven, low-grade biomass resources for conversion in Pyroneer systems. The technical assessment is conducted by comparing the results from a series of physical-mechanical and thermochemical experiments to a set of proven references. The technical assessment is supplemented by an evaluation of practical application and overall energy balance. Applying the developed method to 4 references and 18 unproven low-grade potential fuels, indicated that one of these unproven candidates was most likely unsuited for Pyroneer gasification, 5 of the candidates looked highly problematic, 5 of the candidates looked very promising and 7 of the candidates ranged in between the highly problematic and the very promising.

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1. Introduction

In Denmark, wood pellets are used more and more to substitute coal in existing Combined Heat and Power (CHP) infrastructure. This approach will decrease dependency on fossil fuels and greenhouse gas emissions in the Danish energy sector. However, the biomass resource is limited, and especially the high quality wood resource is stressed by increased utilization in small and large scale energy and material systems around the world. To be able to continue the substitution of coal with renewable biomass, suitable conversion systems need to be introduced that can handle biomass resources of lower quality.

The Pyroneer gasification platform is such a system. The process is currently implemented in a 6 MW demonstration plant at Asnæs power plant in Kalundborg, Denmark, as well as in a 100 kW pilot scale plant at the Technical University of Denmark at Risø, Roskilde, Denmark.

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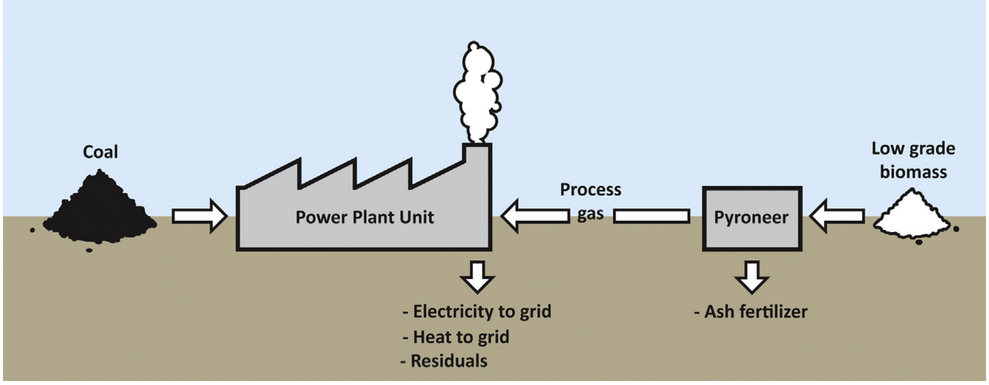

Fig. 1 – **Integration of Pyroneer gasifiers in existing coal based energy infrastructure.**

The technology is characterized as highly fuel flexible, robust and relatively inexpensive compared to other similar conversion platforms [1]. The integration of Pyroneer plants in existing coal based energy conversion infrastructure is illustrated in Fig. 1.

The reference fuel of the current generation of Pyroneer plants is straw – loose or in pellets, but the process has also been proven on even more problematic fuels like digested manure fibers and dried waste water sludge. The Pyroneer gasification process is a Low Temperature Circulating Fluid Bed (LT-CFB) gasifier. It operates at maximum temperatures of around 750 °C and thus largely avoids ash melting due to two related mechanisms [1–3]. First of all, due to the low operating temperatures, many common inorganic ash constituents like K, P and most Cl can be maintained in a solid state in the ash [3]. Secondly, the low temperature and reducing atmosphere prevent fast conversion of fixed carbon, and the ashes are therefore rich in carbon throughout the process. This mechanism has been studied by e.g. Kurkela et al., in 1996 and Skrifvars et al., in 1996 who describe a relation between the completeness of the fuel carbon conversion and the rate of ash deposit formation [4,5]. An illustration of the LT-CFB gasification concept is provided in Fig. 2.

The aim of this work is to develop a simple method for first hand screening of potential low-grade fuels for Pyroneer gasification systems as well as to test this method on a range of biomass and waste resources of varying quality and origin. Characterization of various biomasses and wastes for use in gasification systems have been conducted previously in published literature. The method varies from study to study regarding the assessed conversion platform, the fuel characteristics and the biomass resources included. A short review study on the matter can be found in literature [6]. In the present work, it is attempted to provide a relatively simple method dedicated for initial screening and characterization of potential low-grade fuels for the Pyroneer LT-CFB gasification process.

2. Method

2.1. *Selection criteria*

A list of questions relevant for successful LT-CFB gasification was prepared to set guidelines for the experimental work. The questions were related to the preparation of the potential fuels as well as to the technical feasibility of the actual conversion. The list of questions was as follows:

- Is transportation/handling/feeding problematic due to low energy density per weight or volume?

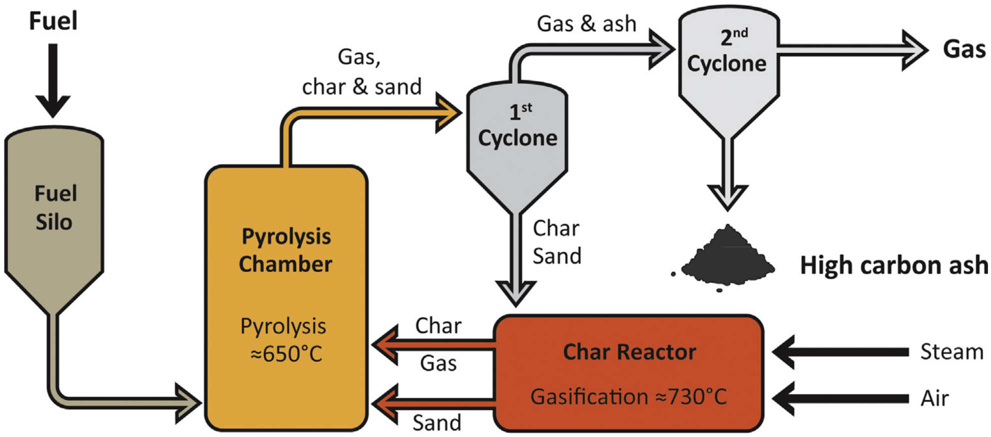

Fig. 2 – **LT-CFB gasification flow sheet diagram.**

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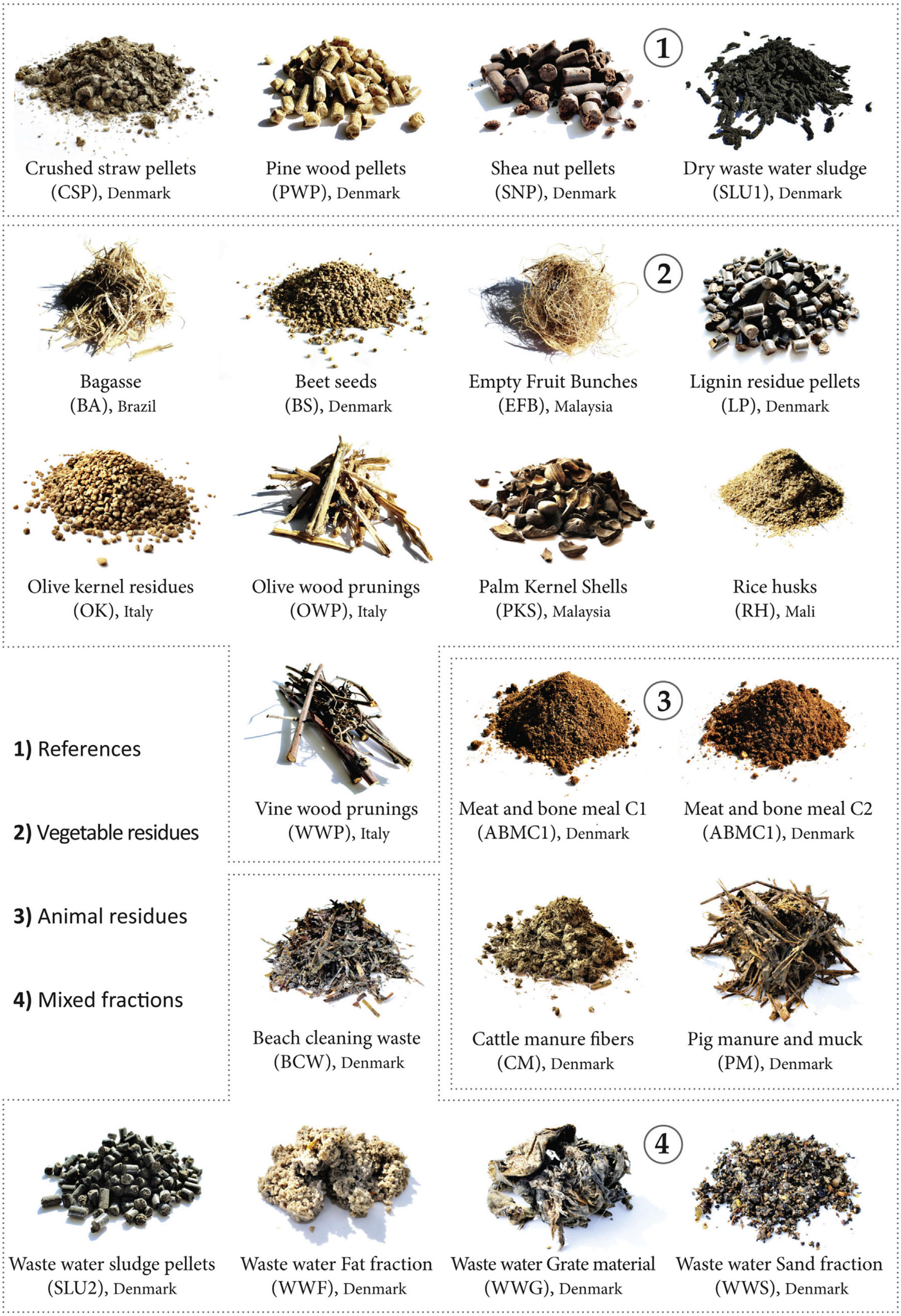

Crushed straw pellets
(CSP), Denmark

Pine wood pellets
(PWP), Denmark

Shea nut pellets
(SNP), Denmark

Dry waste water sludge
(SLU1), Denmark

Bagasse
(BA), Brazil

Beet seeds
(BS), Denmark

Empty Fruit Bunches
(EFB), Malaysia

Lignin residue pellets
(LP), Denmark

Olive kernel residues
(OK), Italy

Olive wood prunings
(OWP), Italy

Palm Kernel Shells
(PKS), Malaysia

Rice husks
(RH), Mali

1) References

2) Vegetable residues

3) Animal residues

4) Mixed fractions

Vine wood prunings
(WWP), Italy

Meat and bone meal C1
(ABMC1), Denmark

Meat and bone meal C2
(ABMC1), Denmark

Beach cleaning waste
(BCW), Denmark

Cattle manure fibers
(CM), Denmark

Pig manure and muck
(PM), Denmark

Waste water sludge pellets
(SLU2), Denmark

Waste water Fat fraction
(WWF), Denmark

Waste water Grate material
(WWG), Denmark

Waste water Sand fraction
(WWS), Denmark

Fig. 3 – Pictures of sub-samples as received.

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- How severe are energy requirements for transportation, drying and grinding?
- What is the content of large stones/glass/metal?
- How reactive is the char in a reducing atmosphere at 750 °C?
- Is the size of reference char reactors (i.e. straw systems) reasonable for the combination of char reactivity and char content in the assessed fuel?
- Is the ratio between energy content in char and volatiles from pyrolysis reasonable for efficient LT-CFB gasification?
- Are there severe agglomeration/char-sticking issues in pyrolysis at 650 °C?
- Are there severe ash sintering issues in steam/air at 750 °C?
- How much of the ash is volatilized at 750 °C?
- Do char and ash densities pose any potential problems in relation to cyclone performance and long term changes in bed density and circulation?
- What is the potential production of electricity and heat from the thermal conversion system (including power plant block)?

The following set of experiments was conducted to answer the questions above:

- Proximate analysis.
- Heating value assessment of fuel and char.
- Bulk density assessment of fuel, char and ash.
- Grinding energy assessment.
- Reactivity measurements.
- Char sticking and agglomeration assessment.
- Ash sticking, sintering/agglomeration and vaporization assessment.

For each indicator the results are compared to a set of 4 references. If the sample performs as well as one of the references on all characteristics, the fuel is assumed to be a suitable fuel. However, the sample may perform worse than the references on some indicators and still have potential for further assessment for conversion in Pyroneer based energy systems. This is discussed further in section 3.

2.2. *Selection of references and potential unproven fuels*

Straw is the primary reference of the Pyroneer conversion platform. However, the gasifier has also been proven on e.g. shea nut residues and dried waste water sludge from the waste water treatment facility Randers Centralrenseanlæg in Randers, Denmark. Samples of these fuels were collected for use as reference. In addition to the proven fuels, Danish pine wood pellets were also included in the reference as a representative of the highest quality biomass fuels.

The unproven fuel samples are selected within three categories and from domestic and foreign resources to achieve as wide a range of characteristics as possible. The three categories are: Vegetable Residues, Animal Residues and a Mixed Fraction including various inhomogeneous waste fractions and dry waste water sludge pellets. Pictures of all the collected samples as they were received are provided in Fig. 3. These pictures should aid in the understanding of particle size and structure as well as the level of homogeneity of the different samples.

All samples were collected in February and March 2014. The samples were obtained by curtesy of many different suppliers and producers within agriculture, agro-industry, bio-energy production or waste management. Some of the samples have key characteristics related to their origin. These are described in short below:

- The characteristics of all samples from waste water treatment facilities (SLU1 + 2, WWF, WWG & WWS) are likely to change significantly with season and the geography and demography surrounding the waste water treatment facility.
- The characteristics of the Beach Cleaning Waste (BCW) is also expected to change with the season. This material is collected by tractor by the Danish Municipality of Solrød to improve the touristic quality of the shoreline and beaches.
- Vine Wood Pruning (VWP) were cut and collected manually by the workers at the vineyard in Tuscany.
- The Olive Wood Pruning (OWP) has been cut, collected and crushed at the plantation in Tuscany.
- Do to the oil production process, the Palm Kernel Shell (PKS) sample assessed had a very high content of NaCl reducing its applicability in conventional incineration systems.
- The Cattle Manure fibers (CM) were produced on a dairy farm by mechanical dewatering of cattle manure by use of a screw press.
- The Pig Manure and muck sample (PM) was passively dewatered in pig stables on multi-layered floors with sieve and membrane systems.
- The animal meat and bone meal samples (ABMC1 + 2) are from a Danish bio-diesel production facility. The categories 1 and 2 relate to the risk assessment – and thus the potential use, of the material by EU standards.

The characteristics of the remaining samples are assumed to be more constant and less dependent on the specific time of sampling and place/process of origin.

2.3. *Experimental procedures*

The experimental procedures used in the assessment are all described below. All experiments are carried out with 2–5 replicates depending on the heterogeneity of the sample.

Content of large unconvertible particles: Defined in the assessment as all unbreakable particles larger than 5 mm. The material is sorted out manually from samples of approximately 500 g. Easily crushable particles are not sorted out as they are assumed to break down during conversion.

Moisture content: Determined by drying several large subsamples of around 500 g in a drying oven at 104 °C for 24 h. The fat trap fraction from waste water treatment required additional drying as well as occasional stirring and was treated for 48 h at 104 °C.

Content of volatile organics in dry samples: Examined by pyrolysis of the dry samples at 600 °C with a heating rate of 6 K min^{-1}, 2 h retention time at maximum temperature and fast cooling. The reactor was flushed continuously with N_2 at

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5 L min^{-1} for the first 20 min, and 2 L min^{-1} for the remaining treatment. Several replicates of 500 g each were used.

Content of fixed carbon and ash in dry char samples from pyrolysis: Examined by annealing of char samples from the pyrolysis. Samples of 100–200 g were used for each repetition. The samples were spread in thin layers (1–2 cm). The annealing was conducted in an oven heated to 550 °C with a heating rate of around 20 K min^{-1}. The annealing proceeded until sample weight was stable for more than 30 min. An air flow of 2 L min^{-1} was supplied to the oven throughout the experiment.

Heating value of biomass and char samples: The heating value was determined as Higher Heating Value (HHV) in a Parr 6300 Bomb Calorimeter with an oxygen supply at 4MPa using small samples of 0.5–0.8 g. Heating value of pyrolysis chars was examined in the same way. The heating value was determined on dry as well as moist basis. However, to take representative sub-samples the materials needed grinding and this was not possible for the collected un-dried samples of Cattle Manure Fibers, Pig Manure Fibers, Beach Cleaning Waste, Waste water Fat fraction, Waste water Grate material and Waste water Sand fraction. Instead, the heating value as received of these samples was estimated using the heating value of the dry sample and the moisture content.

Bulk densities of biomass, char and ash: Bulk densities were determined using measuring cylinders of varying height and diameter and a gentle settling of 0.5 min stomping of the cylinders on a hard surface. In this way, the particles would settle and pack in different ways depending on the dimensions of the cylinder, and a range of reasonable bulk densities for the sample in question could be estimated. Samples of several hundreds of grams up to a few kg were used for measuring bulk densities of dry and moist biomass samples while smaller samples of around 50 g were used for the char densities and just 10–20 g for the ash bulk densities. Char and ash material was grinded prior to the bulk density measurements to obtain particle sizes more similar to those inside the LT-CFB reactors and cyclones. A reference of quartz sand was included as a higher limit for char and ash densities. No pressure was applied to the samples in the cylinders and it is assumed that the average sample densities of large bulk volumes of the fuels would be somewhat higher than the obtained values. The pressure of the sand on char and ash particles in the beds of the LT-CFB is also assumed to increase the densities of chars and ashes compared to the obtained values. However, for comparative purposes the present approach was found suitable.

Grinding energy requirements: It is assumed that grinding of biomass samples with particle minimum diameter larger than 5 mm is required. The energy use for the grinding is assessed by measuring the grinding energy consumption in a Mahlkönig disc grinder or a Wiley knife mill depending on the sample particle size and shape. Grinding energy requirements for downsizing the particles were calculated by integrating the power consumption curve, subtracting the idle state consumption of the grinder and finally dividing the remaining energy use with the sample size. For some samples the available mills were not considered the optimal technology for efficient grinding. However, all grinded samples met the requirements of feed particle minimum diameter below 5 mm.

Reactivity of pyrolysis chars: The reactivity of the pyrolysis chars was examined by converting the chars in a macro TGA (Thermogravimetric Analyzer) at 750 °C in an atmosphere of superheated steam. Char samples of 5–15 g were used for each experiment and repetition. 2 repetitions were made for each biomass and 5 for straw to test the reproducibility of the experiment. The TGA reactor was heated to 750 °C with a heating rate of 10 K min^{-1} under a protective N_2 sweep of 1 L min^{-1}. After stabilizing at maximum temperature, the N_2 atmosphere was replaced by a superheated steam flow of 1 kg h^{-1}. The reactivity was calculated by dividing the first derivative of the normalized weight loss curve by the remaining fraction of organics. Results are obtained in % conversion per minute. Comparing the reactivity after 50% conversion was used as a proxy for the reactivity in general as this was found in literature to be the most comparable section of the conversion curve [7]. Curve approximations were used to determine the first derivative of the weight loss curve.

Char sticking and agglomeration: Char sticking and agglomeration was studied by heating fuel samples in ceramic crucibles to 650 °C with high heating rates of 50 K min^{-1}, an N_2 sweep of 2 L min^{-1} and a retention time at maximum temperature of 4 h. After fast cooling of the samples, the loose chars were brushed out of the crucibles using a soft brush. Subsequently, remaining loose char was removed by supplying a 500 kPa compressed air pressure from 10 cm distance for 0.5 min across the crucible. Char remaining after this treatment was considered non-removable/sticking. Char agglomeration was assessed using the same samples. Under inspiration from ash sintering assessments by Moilanen et al. from 2006 [6], char agglomeration was determined by visual assessment, pressing and breaking of the char particles. The level of agglomeration was categorized as 0, *, ** or *** with 0 being no agglomeration, * being small and easily breakable agglomerates, ** being larger and tougher agglomerates and *** being total agglomeration defined as all particles of a fuel sample merged into one big char particle that was at the same time very hard and difficult to crush.

Ash sticking, sintering/agglomeration and vaporization: Ash characteristics were studied by heating pre-annealed ash samples in ceramic crucibles to 750 °C with high heating rates of around 100 K min^{-1}, in atmospheric air and with a retention time at maximum temperature of 4 h. After fast cooling of the samples, the samples were weighted to determine the weight loss of the samples during the heat treatment. Subsequently, loose ashes were brushed out of the crucibles using a soft brush and remaining loose ashes were removed by supplying a 500 kPa compressed air pressure from 10 cm distance for 0.5 min across the crucible. Ashes remaining after this treatment were considered non-removable/sticking. Ash sintering/agglomeration was assessed using the same samples. As by Moilanen et al. from 2006, ash sintering was determined by visual assessment, pressing and breaking of the ash particles and comparing to the untreated ash samples. The level of sintering was categorized as 0, *, ** or *** with 0 being no sintering; * slightly sintered; ** moderately sintered and *** completely sintered [6]. Sintering of the residuals from the TGA reactivity experiments was evaluated in the same way. A final qualitative assessment of ash behavior was conducted by visual assessment of steel plates used as bottom in the TGA

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reactor. The same plate was used for both repetitions for each sample, and the severity of fouling and/or corrosion of the plates after char conversion used as a proxy for the aggressiveness of the ashes in steel reactors. After Char conversion (as described under "Reactivity of Pyrolysis chars"), the steel plates were brushed using a soft brush, and afterwards they were cleaned using 500 kPa compressed air from 10 cm distance for 0.5 min.

Transport energy requirements: The following transport distances are used for estimation of transport fuel requirements:

- Domestic dry fractions (sludges, pellets (wood, shea nut, straw and lignin), beet seeds and animal meat- and bone meal): 300 km truck.
- Domestic wet fractions (Manure fibers, beach cleaning waste and waste water treatment fractions of fat, sand and grate material): 100 km truck.
- Brazil (Bagasse): 500 km truck + 12 000 km ship.
- Malaysia (Empty Fruit Bunches and Palm Kernel Shells): 500 km truck + 28 000 km ship.
- Italy (Olive and vine residues): 500 km truck + 1500 km train.
- Mali (Rice Husks): 500 km truck + 500 km train +5000 km ship.

The specific fuel consumption rates for the three types of transport used in assessment of transport energy requirements are 2.67 MJ Mg^{-1} km^{-1} for truck transport, 0.19 MJ Mg^{-1} km^{-1} for train transport and 0.14 MJ Mg^{-1} km^{-1} for ship transport [8].

Drying energy requirements: There is a technical maximum water mass fraction of 30% for LT-CFB fuels [1]. Drying energy requirements were estimated using a global latent heat of vaporization of water at 120 °C and standard atmospheric pressure (101 kPa) of 2.3 MJ kg^{-1}, a specific heat capacity of sample dry matter of 3.8 kJ kg^{-1} K^{-1} and a specific heat capacity of moisture of 4.2 kJ kg^{-1} K^{-1}. A global 90% energy efficiency in drying operations was assumed.

Net energy output from thermal conversion: In the gasification process, a 1% thermal loss was assumed from the equipment in addition to the heat- and energy loss in the ash fraction. 2% of the fixed carbon of the fuel was assumed to be present in the ash with a higher heating value of 35 MJ kg^{-1}. The temperature of the ash leaving the gasifier was assumed to be 600 °C and the specific heat capacity of the ash was assumed to be 0.8 kJ kg^{-1} K^{-1}. In the power plant block, 44% electric efficiency of the gas lower heating value was assumed alongside a 5% thermal loss from the system and an assumption about 70% recovery of the heat of vaporization of water in the fuel for heat production. It was furthermore assumed that the total thermal conversion chain use 1.5% of the produced electricity.

3. Results and discussion

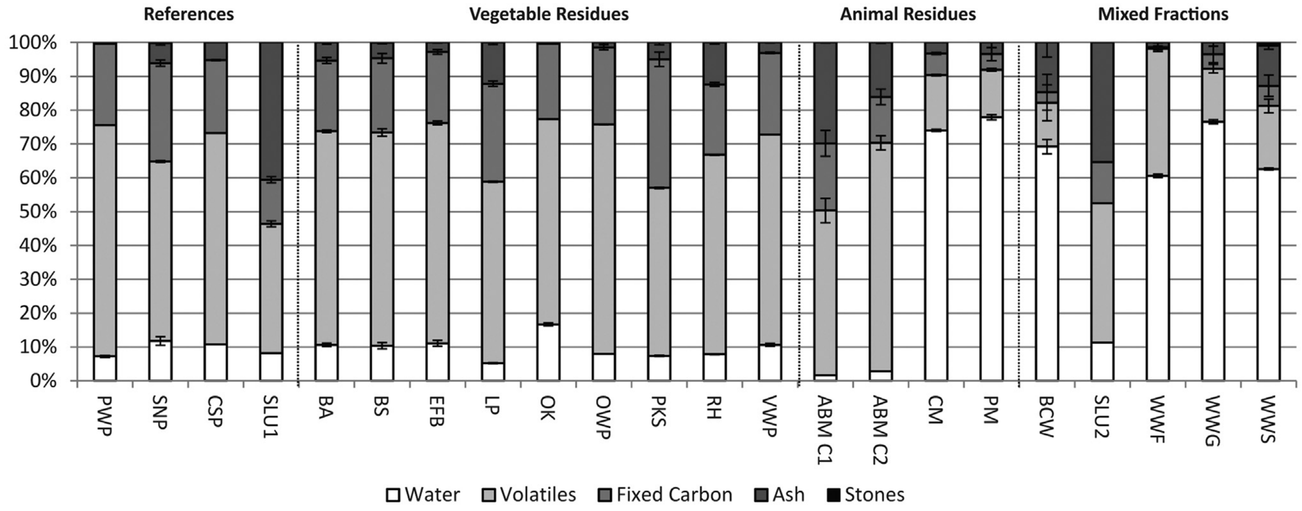
3.1. *Proximate analysis*

The results from the proximate analysis of the fuels as received are presented in Fig. 4.

The most striking difference between the four references and the unproven fuels is related to the moisture content. However, the content of fixed carbon and ash varies significantly as well. The proximate analysis is not used as a direct indicator for suitability of the new fuels, but the results are used on numerous occasions to scale other indicators.

3.2. *Bulk density and energy density assessment*

In Fig. 5, the bulk densities of the assessed fuel samples are presented on dry as well as on as received basis.



PWP: Pine Wood Pellets, **SNP:** Shea Nut Pellets, **CSP:** Crushed Straw Pellets, **SLU1:** Dry Waste Water Sludge | **BA:** Bagasse, **BS:** Beet Seeds, **EFB:** Empty Fruit Bunches, **LP:** Lignin Pellets, **OK:** Olive Kernels, **OWP:** Olive Wood Pruning, **PKS:** Palm Kernel Shells, **RH:** Rice Husks, **VWP:** Vine Wood Pruning | **ABM C1:** Animal Meat- and Bone Meal Catergory 1, **ABM C2:** Animal Meat- and Bone Meal Catergory 2, **CM:** Cattle Manure Fibers, **PM:** Pig Manure Fibers | **BCW:** Beach Cleaning Waste, **SLU2:** Waste Water Sludge Pellets, **WWF:** Waste Water Fat Fraction, **WWG:** Waste Water Grate Material, **WWS:** Waste Water Sand Fraction

Fig. 4 – Proximate analysis of fuel samples as received.

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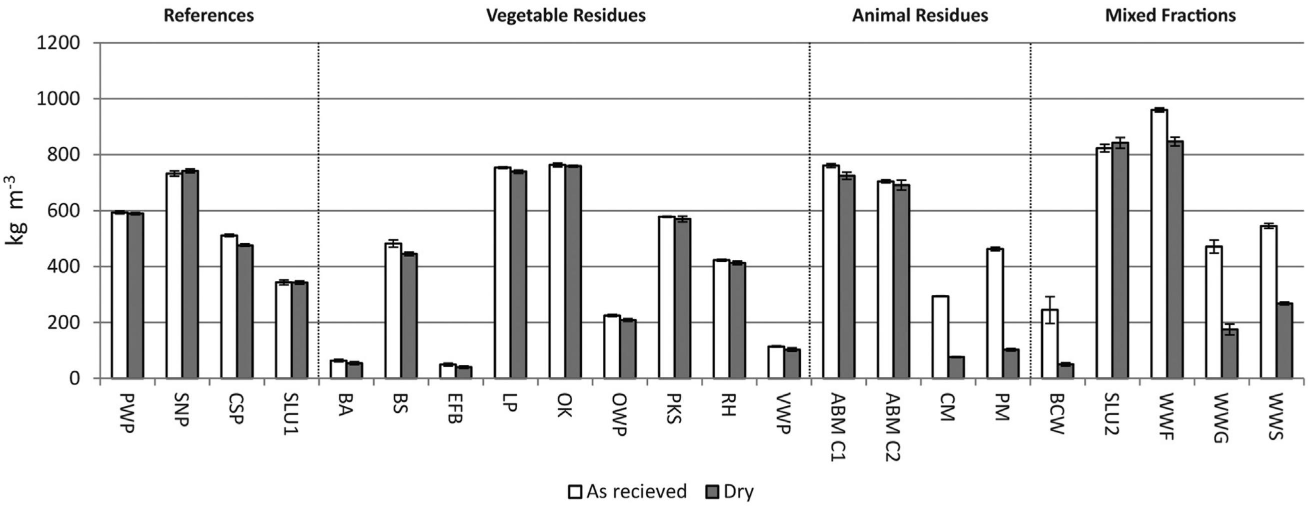

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Fig. 5 – Bulk density of fuel samples – as received and dry.

Energy densities on Higher Heating Value basis are provided in Fig. 6. Results are provided for the samples as received on weight basis as well as on volume basis where the weight based results are combined with the bulk density results from Fig. 5. Results for very moist samples (more than 60% moisture) have been recalculated from measurements on dry basis combined with moisture content data from Fig. 4.

A significant range in energy densities of the reference fuels is observed. On weight base they range from 12.2 to 18.6 with an average around 16 GJ Mg^{-1}. The highest energy density per weight is the pine wood pellets which is 150% of the lowest value – the dry sludge. On volume base the range is even wider going from 4.2 to 12.5 with an average around 9 GJ m^{-3}. The highest volumetric energy density of the shea nut pellets is thus around 3 times the volumetric energy density of the dry sludge.

The energy density results of the unproven fuels indicate that there are two groups of fuels that deviate significantly from the references. The first group consists of CM, PM, BCW, WWG and WWS and they all have significantly lower energy density values than all references on weight as well as on volume base. From Fig. 4, it is clear that these issues arise from

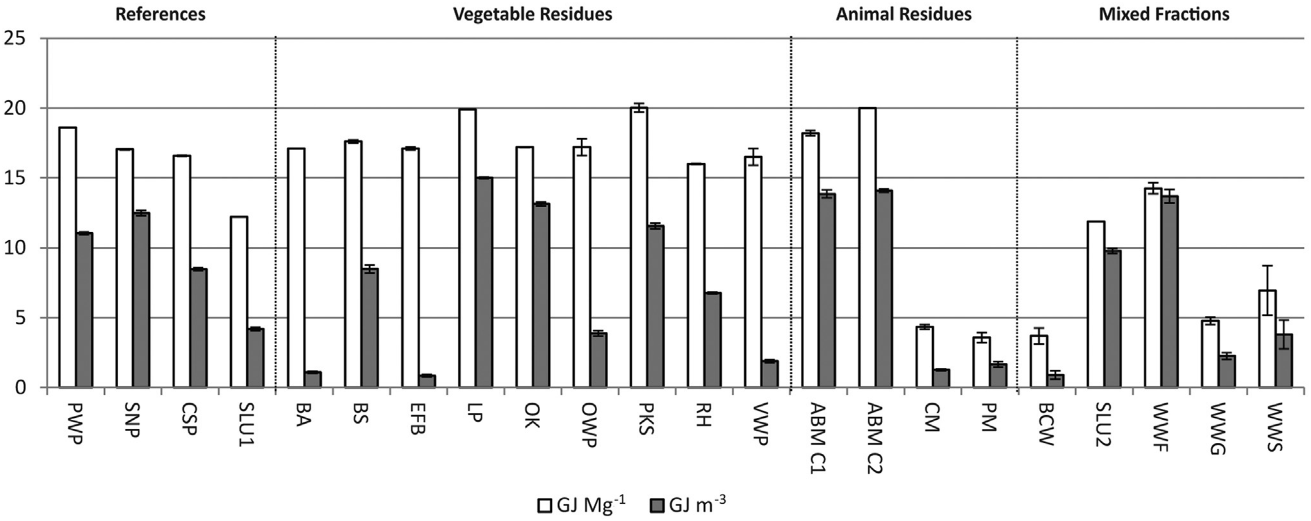

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Fig. 6 – Energy density (HHV) of fuel samples as received – on weight and volume basis.

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very high moisture content on as received basis. This issue could likely be resolved by drying of the fuels prior to feeding, but would still be problematic in relation to efficient transportation and handling. The second group of fuels deviating significantly from the references includes BA, EFB and VWP. These fuels have a high heating value on weight basis, but very low bulk densities and therefore very low energy density on volume basis. The average volume based energy density of these three fuels is around 1/7th of the average reference and less than 1/3rd of the lowest reference value. This can be problematic in relation to transportation and feeding as the feeding system is unlikely to handle fuels that differ this much in volumetric requirements. Transportation, handling and feeding of these fuels could probably benefit from densification via torrefaction and/or pelletization [9–11]. Based on the results from the bulk density assessment of the dry fuels in Fig. 5, it is found likely that dry CM, PM, BCW and to some extent WWG, also could benefit from densification prior to feeding in reference fuel feeding systems.

3.3. *Energy content of pyrolysis products*

The next step in the technical assessment of the new fuels is an assessment of the energy content of the pyrolysis products. A certain minimum of char is required to generate sufficient heat for the pyrolysis. The results are presented in Fig. 7.

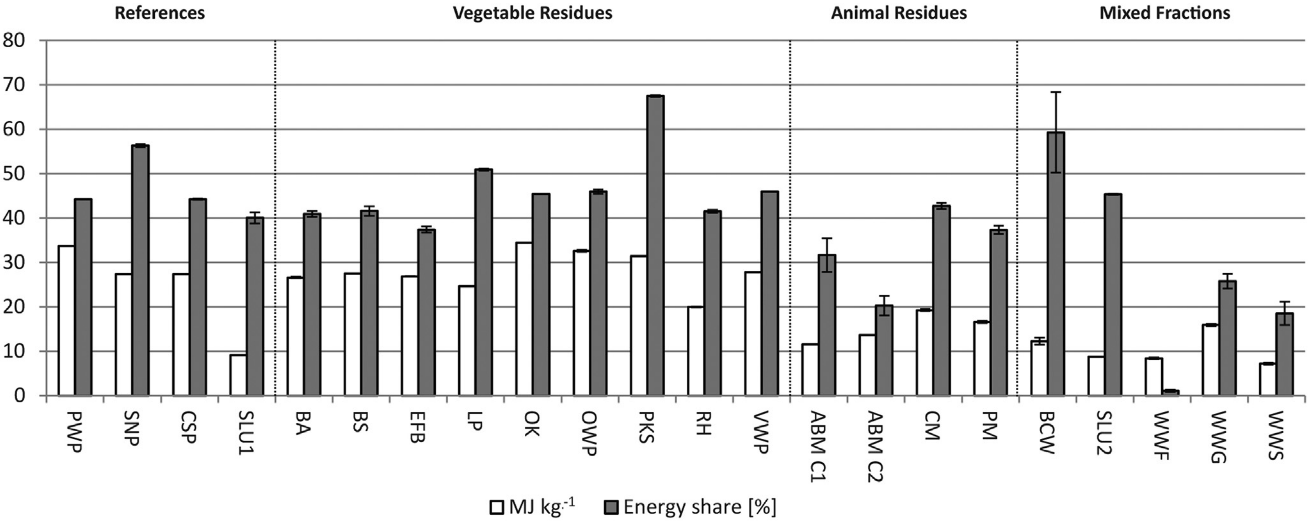
From the results in Fig. 7, it is evident that the char energy share of especially WWF – but also to some extent WWS, WWG and ABM C2, could be problematic in regard to conversion in reference LT-CFB straw based plants. To assess the matter further, the energy requirements inside the pyrolysis reactor were estimated and compared to the potential heat generation in the char reactor. The following assumptions were used in the assessment:

- Specific heat capacity of water: 4.18 kJ kg^{-1} K^{-1}.
- Heat of vaporization of water at 120 °C and at standard atmospheric pressure of 2.3 kJ kg^{-1}.
- Pyrolysis reactor inlet and outlet temperatures: 25 °C and 650 °C respectively.
- Energy requirements for heating dry matter: 600 kJ kg^{-1} [12].
- Energy requirements for endothermic reactions: 200 kJ kg^{-1} [12].
- Carbon loss to ash fraction: 2% of the mass of fixed carbon in feed.

These generalized assumptions were combined with information about proximate analysis composition of the fuels (dried to max 30% moisture) as well as char heating value measurements to obtain Char Sufficiency Ratio values that describes the energy content in the available char relative to the estimated energy requirements in the pyrolysis reactor. The results are provided in Fig. 8. Keeping in mind that the calculations are rough estimations the Char Sufficiency Ratio should be significantly higher than one to surely satisfy energy requirements for the pyrolysis. If 1.5 is used as a threshold it is evident that WWF and WWS fail to comply with these restrictions and WWG is also close (1.8). All reference fuels have ratios of 4–7.

3.4. *Char and ash bulk density assessment*

Very low char densities are assumed to influence cyclone performance leading to reduced energy efficiency while very high ash densities are expected to facilitate ash accumulation in the bed and subsequent changes in the bed density, fluidization- and circulation characteristics. The bulk densities of char and ash are presented in Fig. 9 alongside results from a sample of clean quartz sand which is a common bed material in LT-CFB gasifiers.



PWP: Pine Wood Pellets, **SNP:** Shea Nut Pellets, **CSP:** Crushed Straw Pellets, **SLU1:** Dry Waste Water Sludge | **BA:** Bagasse, **BS:** Beet Seeds, **EFB:** Empty Fruit Bunches, **LP:** Lignin Pellets, **OK:** Olive Kernels, **OWP:** Olive Wood Pruning, **PKS:** Palm Kernel Shells, **RH:** Rice Husks, **VWP:** Vine Wood Pruning | **ABM C1:** Animal Meat- and Bone Meal Catergory 1, **ABM C2:** Animal Meat- and Bone Meal Catergory 2, **CM:** Cattle Manure Fibers, **PM:** Pig Manure Fibers | **BCW:** Beach Cleaning Waste, **SLU2:** Waste Water Sludge Pellets, **WWF:** Waste Water Fat Fraction, **WWG:** Waste Water Grate Material, **WWS:** Waste Water Sand Fraction

Fig. 7 – Char Higher Heating Value (MJ kg^{-1}) and char energy content in % of fuel energy content at maximum 30% moisture.

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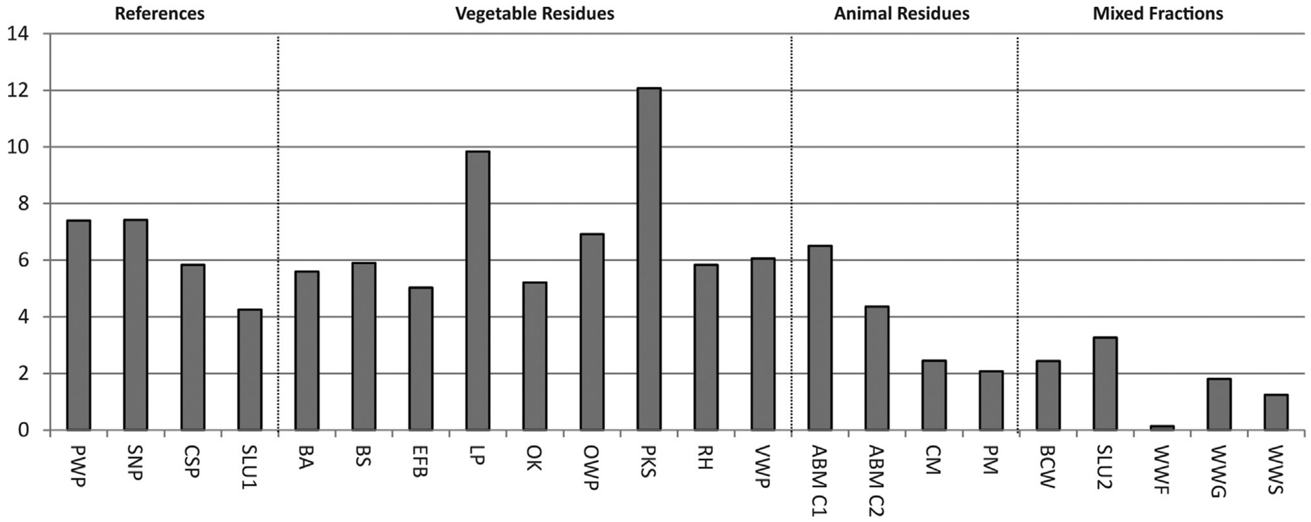

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Fig. 8 – Char sufficiency ratios describing the available energy in the char fraction divided by the energy requirements in the pyrolysis reactor.

The results show a wide range in the reference ash densities and a much narrower range in the char densities. All unproven fuel ash density results are placed in the range between the lowest reference ash density (PWP) and the quartz sand density. Based on these results there is no apparent risk of critical long term changes in bed density from operation on the assessed fuels. However, as mentioned in the method section, the ash bulk density assessments may be underestimating the actual values in the system due to the increased particle pressure from the bed material.

The main concern related to the char density is that very light char fractions could have difficulties settling in the reference system straw char cyclones leading to reduced cyclone performance, higher carbon loss and thus reduced thermal efficiency. The lowest reference char density is CSP around 550 kg m^{-3}. 11 of the unproven fuels have lower char densities than CSP, and four of these (BA, EFB, VWP and CM) have char densities around half (or lower) than CSP. No experiments have been performed to verify this risk, but a rough assessment using general cyclone theory and data from a

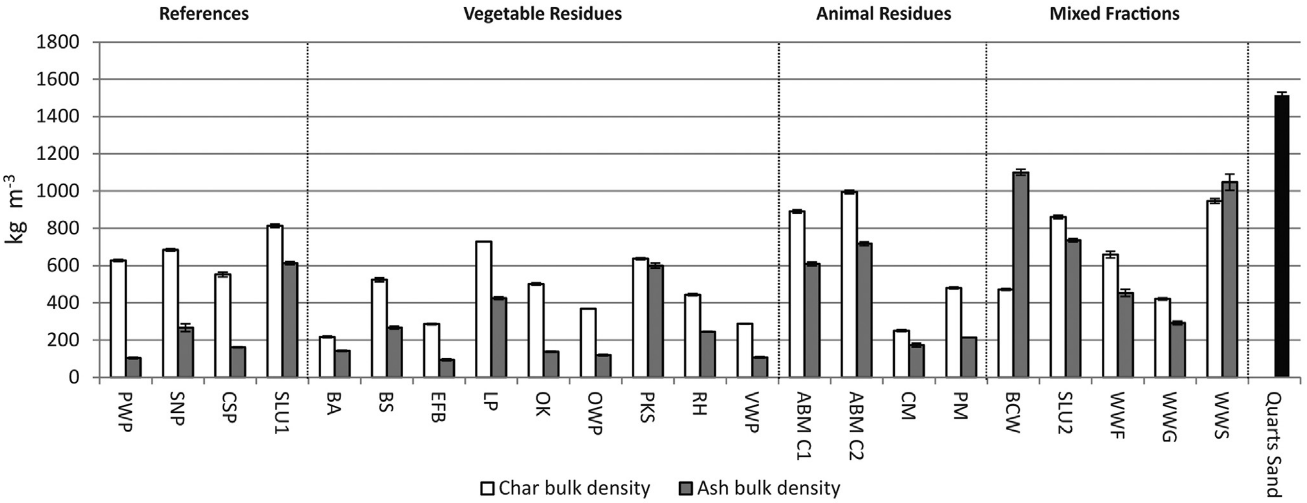

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Fig. 9 – Bulk density of char and ash samples.

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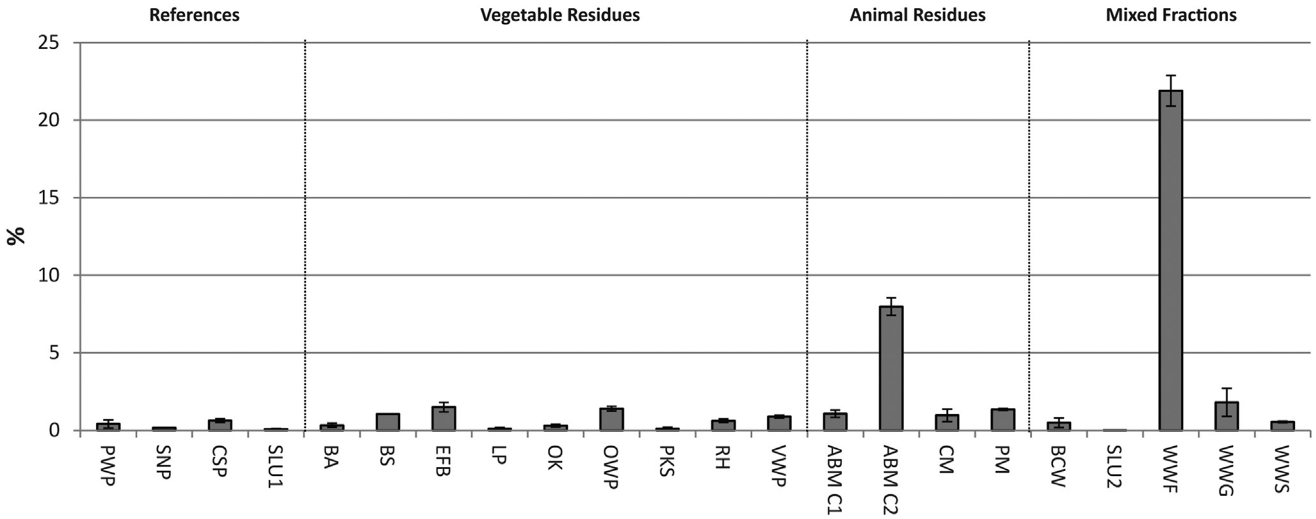

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Fig. 10 – Char sticking in pyrolysis. Results given as the mass of char sticking after cleaning measured in % of initial sample mass.

500 kW LT-CFB suggests around 10% decrease in cyclone performance when decreasing char density from 550 kg m^{-3} (CSP) to 217 kg m^{-3} (worst case, BA) [3].

3.5. *Char sticking/fouling and agglomeration in pyrolysis reactor*

Results from the quantitative char sticking/fouling assessment are presented in Fig. 10 and Fig. 11 alongside results from the more qualitative char agglomeration assessment in Table 1. There is no clear general correlation between the results of the char sticking assessment and the char agglomeration assessment, and both indicators thus need to be included in the technical feasibility assessment. However, it is evident that the four references show very little or no char sticking/fouling and no agglomeration tendencies, and the severity of these characteristics is therefore largely unknown. Based on this observation, it is decided to question the suitability of the following unproven fuels in LT-CFB conversion systems: BS, ABM C1 + 2, WWF and WWG.

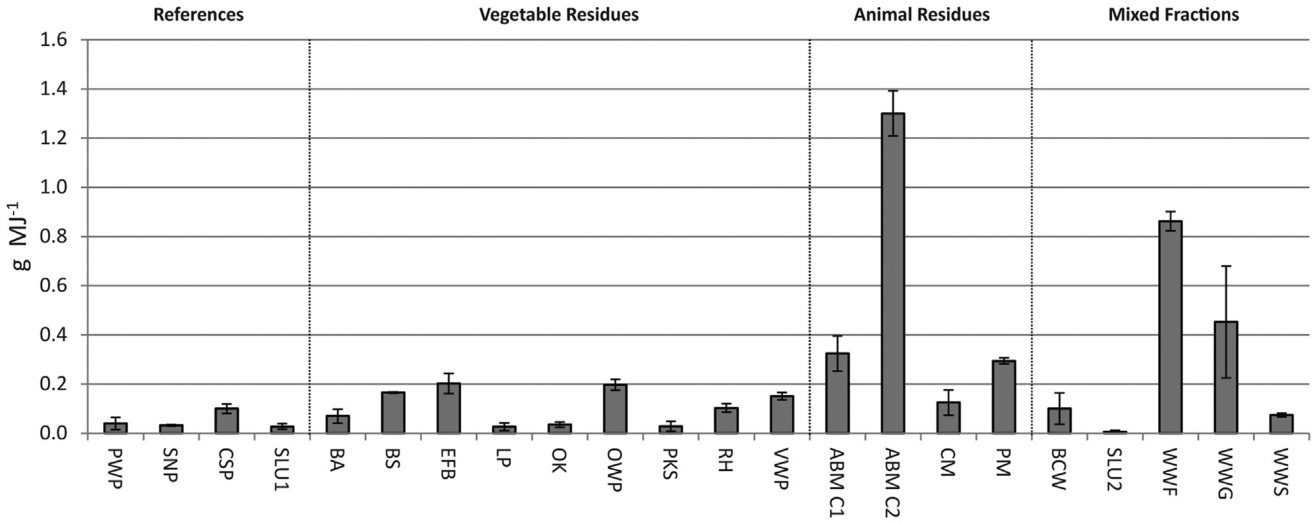

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Fig. 11 – Char sticking in pyrolysis. Results given as g char sticking after cleaning per MJ biomass fuel converted.

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Table 1 – Char agglomeration in 650 °C, N_2 atmosphere.

References		Animal residues	
Pine wood pellets	0	Animal meat- and bone meal cat. 1	***
Shea nut pellets	0	Animal meat- and bone meal cat. 2	***
Crushed straw pellets	0	Cattle manure fibres	0
Dry waste water sludge	0	Pig manure fibres	0
Vegetable residues		**Mixed waste residues**	
Bagasse	0	Beach cleaning waste	0
Beet seeds	**	Waste water sludge pellets	0
Empty fruit bunches	0	Waste water fat fraction	*
Lignin pellets	0	Waste water grate material	0
Olive kernels	0	Waste water sand fraction	*
Olive wood pruning	0		
Palm kernel shells	0		
Rice husks	*		
Vine wood pruning	0		

0: no agglomeration, *: small and easily breakable agglomerates, **: larger and tougher agglomerates, ***: total agglomeration, one particle.

3.6. *Ash sticking/fouling, vaporization and sintering in char reactor*

The ash behavior is investigated in conditions simulating the char reactor atmosphere in different ways. In Fig. 12 and Fig. 13 the results from the quantitative assessment of ash sticking/fouling and ash vaporization in 750 °C, air are presented. The reference results indicate that slight ash sticking as well as substantial ash vaporization is not necessarily problematic. In regard to the ash vaporization, clarification of the severity of this characteristic would require detailed ash analysis which is beyond the scope of this work. In relation to ash sticking, it is important to remember that this assessment of ash sintering was made in a worst case setting with carbon free ashes and a retention time of 4 h. This is not likely to occur in the reducing atmosphere of the LT-CFB char reactor, as the ash fraction from the secondary cyclone usually always holds a significant amount of residual carbon [1–3,13]. However, the ash sticking behavior of the PKS sample (and to some extent SLU2) is striking and calls for caution if attempting conversion of this fuel. The high NaCl content of the assessed PKS sample is expected to have significant influence on the ash melting tendencies.

A set of more qualitative results related to potential ash sintering is provided in Table 2 and Table 3 as well as in Fig. 14. The results are from experimental assessment of the behavior of carbon free ashes in air as well as the behavior of pyrolysis chars converted in saturated steam.

Judging from the reference behavior alone, it is assumed that slight sintering of ash in air as well as severe sintering of exposed ash in steam is unproblematic. The SLU1 is the only reference fuel that shows no indication of ash sintering, fouling or corrosion on TGA steel plates. PWP and SNP show slight ash sintering in air, severe ash sintering in steam and some corrosion (PWP) and fouling (SNP) of the TGA steel plates. CSP also show some sintering in air, but the char sample was unconverted in the TGA. However, significant changes to the color and texture of the TGA steel plate were still observed.

Assessment of the results for the unproven fuels indicates severe risk of ash sintering in air of the samples BS, EFB, LP, OK, OWP, PKS and VWP. In steam conversion of chars the most pronounced sintering occurred for samples BS, EFB, VWP, AMB C1 + 2 and BCW. Assessment of the steel plates from the TGA experiment show fouling tendencies for BS, OK, VWP, ABMC1 + 2, CM and BCW and potential corrosion of the steel when converting OWP and especially VWP.

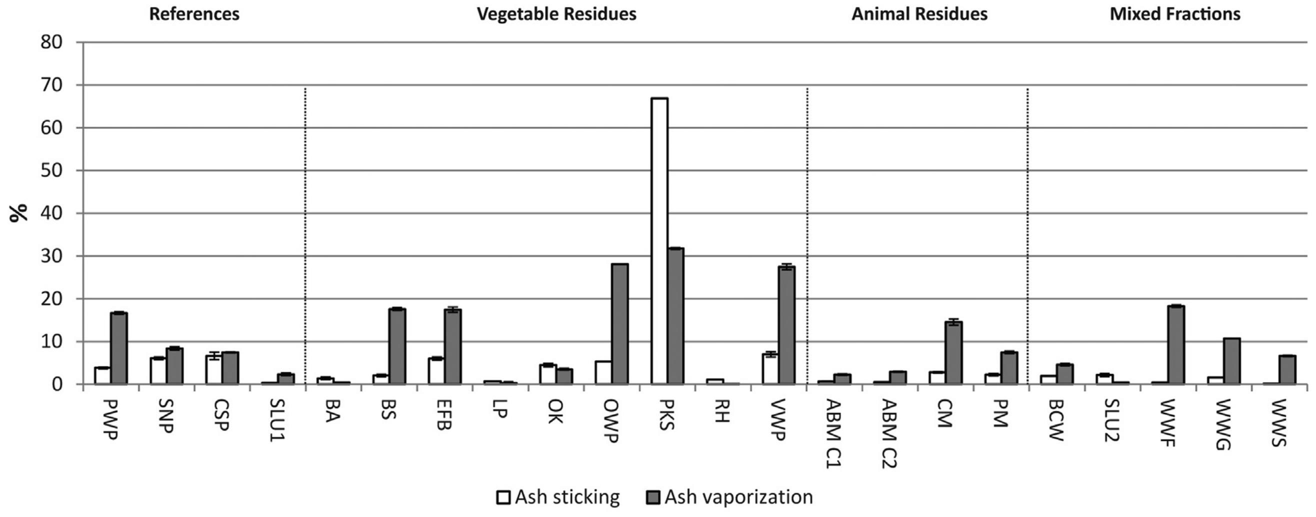

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Fig. 12 – Ash sticking and vaporization at 750 °C in air. Determined as mass vaporized or sticking after cleaning and measured in % of initial sample mass.

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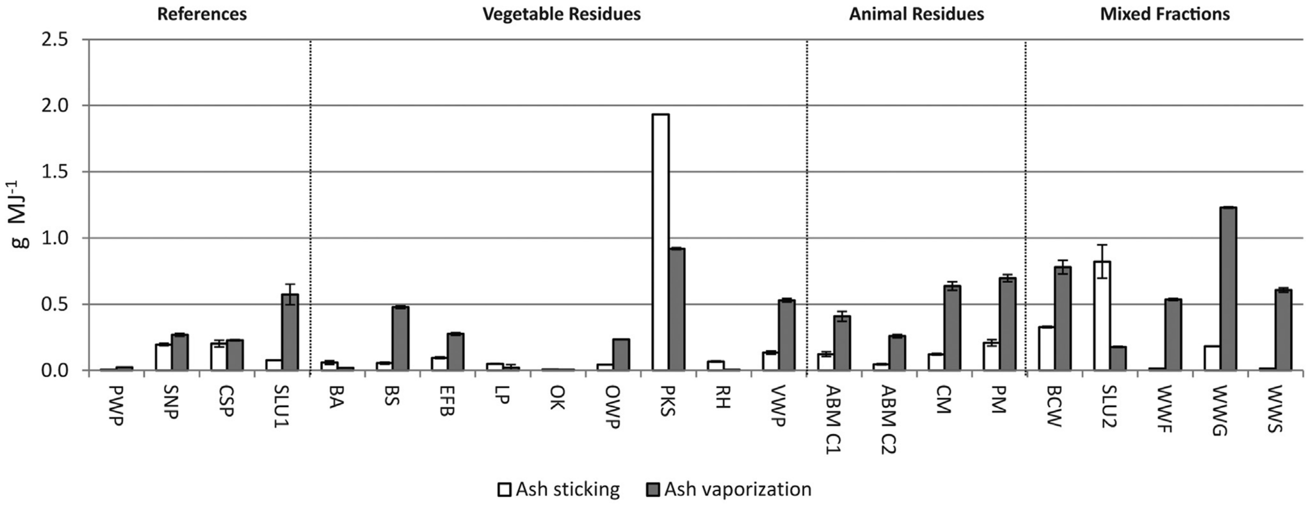

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Fig. 13 – Ash sticking and vaporization at 750 °C in air provided as g ash vaporized or sticking after cleaning per MJ biomass fuel converted.

Despite the significant negative results of the ash sintering experiments, the current assessment is not sufficient to judge a fuel technically feasible or infeasible. A detailed literature study by Moilanen from 2006 about the difference between ash sintering characteristics and actual gasifier performance suggest that differences are significant and vary with method, fuel and gasification platform [6]. Van der Drift & Olsen predicted ash agglomeration tendencies and ash sintering behavior in great detail in a study from 1999 and one of the conclusions was that in fluidized bed experiments all parameters affect the agglomeration incl. process design, fuel-bed material interactions, volatilization and condensation, shear forces, temperature homogeneity and accumulation. They therefore recommended that laboratory experiments and facilities were used mainly to compare fuels and to identify potential risks and solutions. They also recommended to take great care when drawing conclusions for full-scale application based on laboratory scale experiments [14].

3.7. Reactivity of pyrolysis chars

The reactivity of the pyrolysis chars is measured in order to identify potential discrepancies between reference char reactor size and the char conversion rate and char quantity of

Table 2 – Ash sintering in 750 °C, air.

References		Animal residues	
Pine wood pellets	*	Animal meat- and bone meal cat. 1	0
Shea nut pellets	*	Animal meat- and bone meal cat. 2	0
Crushed straw pellets	*	Cattle manure fibres	0
Dry waste water sludge	0	Pig manure fibres	*
Vegetable residues		**Mixed waste residues**	
Bagasse	0	Beach cleaning waste	*
Beet seeds	***	Waste water sludge pellets	0
Empty fruit bunches	**	Waste water fat fraction	n.a.
Lignin pellets	***	Waste water grate material	0
Olive kernels	**	Waste water sand fraction	0
Olive wood pruning	**		
Palm kernel shells	***		
Rice husks	0		
Vine wood pruning	**		

n. a.: not assessed. 0: no sintering; *: slightly sintered; **: moderately sintered, ***: completely sintered.

Table 3 – Sintering of residuals from TGA char conversion in 750 °C, steam.

References		Animal residues	
Pine wood pellets	**	Animal meat- and bone meal cat. 1	***
Shea nut pellets	***	Animal meat- and bone meal cat. 2	***
Crushed straw pellets	@	Cattle manure fibres	0
Dry waste water sludge	@	Pig manure fibres	*
Vegetable residues		**Mixed waste residues**	
Bagasse	@	Beach cleaning waste	**
Beet seeds	**	Waste water sludge pellets	@
Empty fruit bunches	@	Waste water fat fraction	n.a.
Lignin pellets	*	Waste water grate material	0
Olive kernels	*	Waste water sand fraction	0
Olive wood pruning	@		
Palm kernel shells	@		
Rice husks	**		
Vine wood pruning	**		

n. a.: not assessed. @: incomplete conversion, 0: no sintering; *: slightly sintered; **: moderately sintered, ***: completely sintered.

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the unproven fuels. In addition, the char reactivity is an important parameter in the interpretation of the ash sintering properties of the ash. Results from the reactivity studies are provided in Fig. 15. The results are given as reactivity measures in the point after 50% conversion (R_{50}) as well as in average reactivity across the first 50% conversion.

In regard to char conversion reactor dimensions it is observed that the reactivity of LP, OK, PKS and RH is very low.

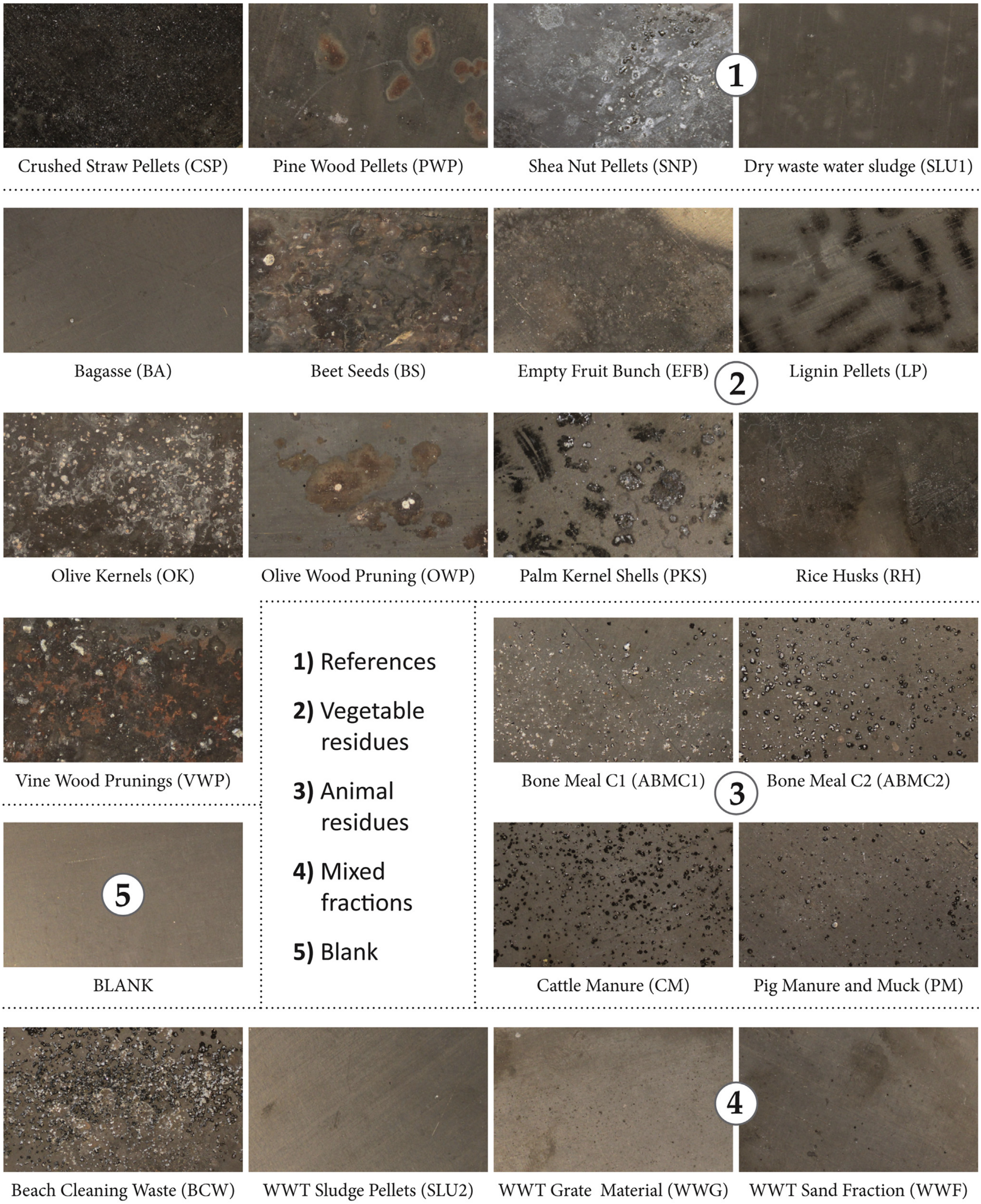

Fig. 14 – Visual assessment of TGA steel disc surfaces.

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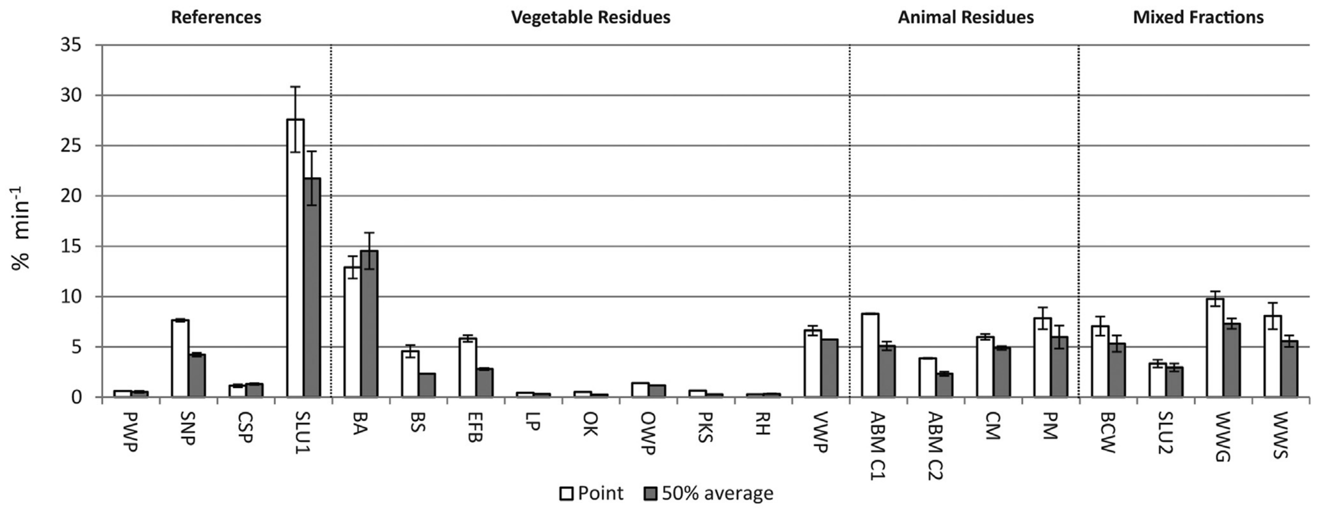

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Fig. 15 – Char reactivity in 750 °C, steam. WWF not assessed. Results as % organics converted per minute provided as a point result at 50% conversion as well as an average conversion rate across 0–50% conversion.

Relative to the primary reference CSP, the reactivity values are 0.3–0.4 for LP, 0.25–0.5 for OK, 0.27–0.6 for PKS and 0.2–0.3 for RH. At the same time, the proximate analysis provides information about the content of fixed carbon in the fuel. Relative to CSP the level of fixed carbon is 1.3, 1.0, 1.8 and 1.0 for LP, OK, PKS and RH respectively. Combining these findings could indicate potential problems when converting these fuels on reference dimension systems. A solution can be to purge more carbon to the ash fraction, but that would lead to a decrease in thermal efficiency of the system. Another solution could be to include the requirement for increased flexibility in the dimensioning of the reference reactor or increase the supply of air.

Related to char reactivity and ash sintering, sticking and vaporization issues, a low reactivity can be a beneficial characteristic of a fuel. In 1996, Kurkela et al. and Skrifvars et al. looked into the matter and concluded among other things the following correlations [4–6]:

- The carbon conversion rate and completeness is dependent on the reactivity of the pyrolysis chars and the system operating conditions.
- High reactivity facilitates a high rate of ash formation leading to a high rate of ash deposit formation.
- In systems with incomplete char conversion ash sintering is largely prevented.

These mechanisms could explain why ashes from the reference fuels PWP and SNP sinter (especially in steam), without leading to significant operational problems. PWP has very low char reactivity and a high fixed C content and the SNP has a high reactivity and very high fixed C content. In this specific regard, highly suitable fuels thus seem to have either minimum sintering tendencies, low reactivity, high fixed C content or incomplete carbon conversion.

There are many factors that influence reactivity measures, and for this reason, the results are applicable mainly for

Table 4 – Electricity required to grind samples to below 5 mm n.a. = Not assessed.

References	As received	Dry
Pine Wood Pellets	22 ± 0	15 ± 0
Shea Nut Pellets	10 ± 0	4 ± 0
Crushed Straw Pellets	4 ± 0	4 ± 0
Dry Waste Water Sludge	4 ± 0	2 ± 0
Vegetable residues	**As received**	**Dry**
Bagasse	317 ± 35	179 ± 16
Beet seeds	5 ± 0	4 ± 0
Empty fruit bunches	432 ± 15	99 ± 9
Lignin pellets	6 ± 0	5 ± 0
Olive kernels	42 ± 1	41 ± 1
Olive wood pruning	305 ± 42	223 ± 67
Palm kernel shells	21 ± 1	21 ± 1
Rice husks	n.a. ± n.a.	n.a. ± n.a.
Vine wood pruning	114 ± 13	105 ± 31
Animal residues	**As received**	**Dry**
Animal meat- and bone meal cat. 1	n.a. ± n.a.	n.a. ± n.a.
Animal meat- and bone meal cat. 2	n.a. ± n.a.	n.a. ± n.a.
Cattle manure fibres	n.a. ± n.a.	n.a. ± n.a.
Pig manure fibres	n.a. ± n.a.	18 ± 2
Mixed waste residues	**As received**	**Dry**
Beach cleaning waste	37 ± 2	8 ± 3
Waste water sludge pellets	4 ± 0	3 ± 0
Waste water fat fraction	n.a. ± n.a.	n.a. ± n.a.
Waste water grate material	n.a. ± n.a.	1198 ± 221
Waste water sand fraction	n.a. ± n.a.	n.a. ± n.a.

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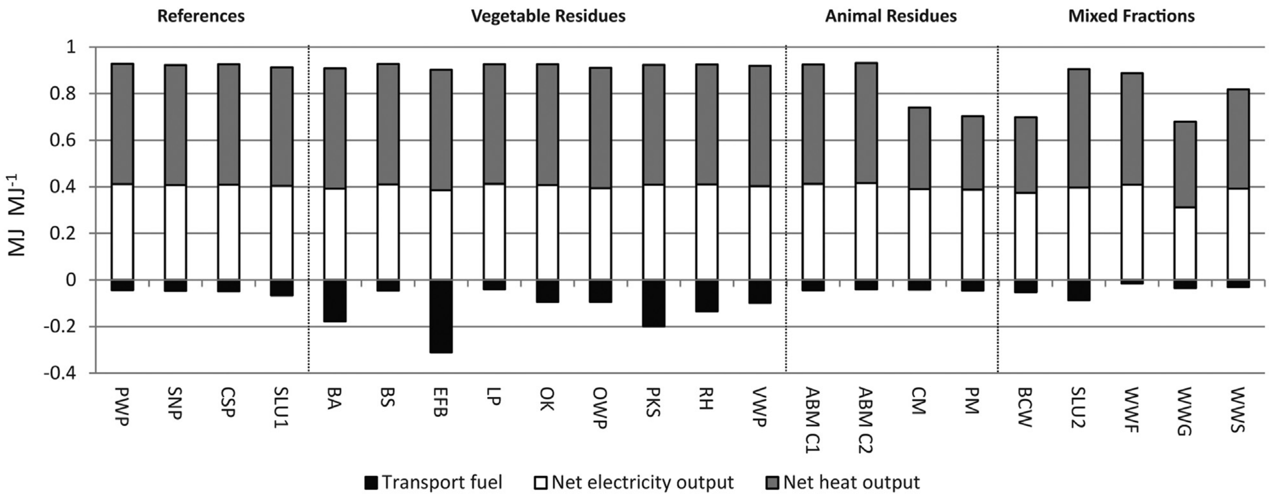

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Fig. 16 – Estimations of transport fuel requirements and net output of electricity and heat. All results in MJ per MJ fuel fired.

comparative measures and there will still be significant differences between the comparative behavior of the assessed fuels in Macro TGA conditions and full-scale LT-CFB systems. For a detailed theoretical and practical investigation of the matter, it is recommended to refer to the PhD study published by Moilanen in 2006 [6].

3.8. Overall energy output and energy yield ratio

The final part of the assessment is an estimation of energy in- and output as well as the energy yield ratio measured as the energy output divided by the energy input. The first part of this assessment is the results from experimental determination of the energy required to grind the fuel samples to particle size range below 5 mm. The results from this assessment are provided in Table 4.

The grinding energy is combined with estimations of drying energy requirements, transport energy requirements and fuel composition and HHV. The main results from the energy balance and yield ratio calculations are provided in Fig. 16 and Fig. 17.

Transport distance, energy density, moisture content, grinding requirements and proximate analysis all influence the results of the energy balance and EROI estimations. BA, EFB, PKS and RH all have significant transportation requirements when assessed for conversion in a Danish energy

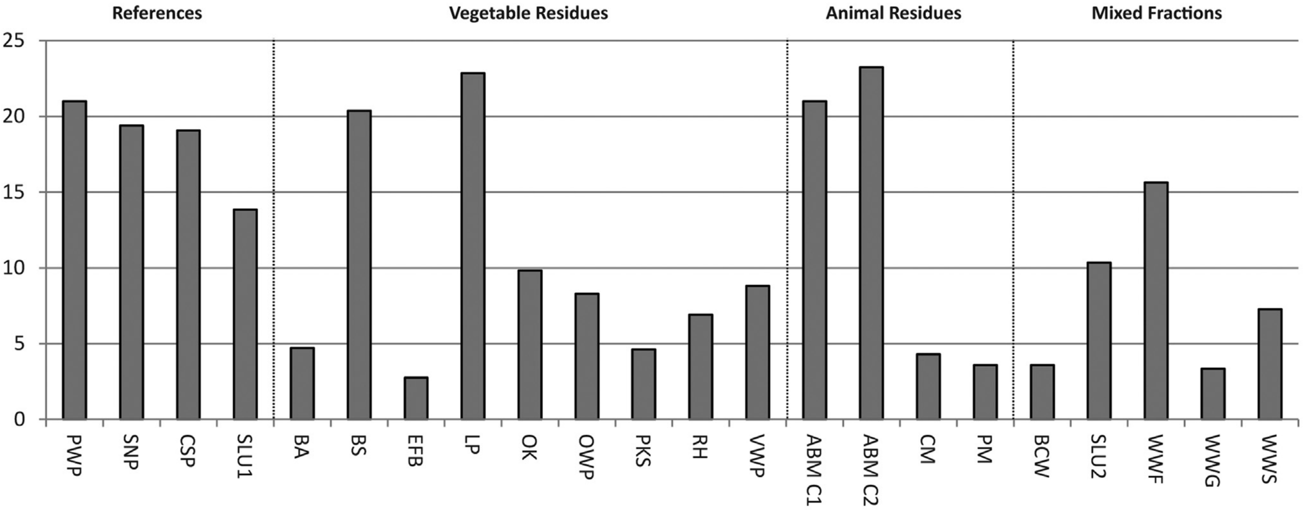

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Fig. 17 – Estimations of the energy return on energy invested (EROI) ratio of the preparation and conversion processes including input and output of transport fuel, heat and electricity.

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system. Conversion of these fuels would benefit greatly from more local systems. CM, PM, BCW, WWG and to some extent WWS all show a decreased output of electricity and heat. The EROI calculations points to the same fuels, but also the Italian residues (OK, OWP and WWP) as well as the dry sludge pellets (SLU2) have energy return ratios below average. In this specific respect the samples BS, LP, ABMC1 + 2 and WWF seem to have the most desirable traits.

3.9. *Summing up*

It is not a simple task to judge about the practical and technical feasibility of converting the assessed fuel candidates in Pyroneer systems. All the unproven fuels showed problematic traits in at least one part of the analysis. However, when the behavior of the proven references was taken into account new potential LT-CFB fuel candidates can be identified – but some are easier to classify than others. The WWF and to some extent WWS have an insufficient carbon content in the char fraction to provide enough energy for the pyrolysis. The next group of candidates that look the most problematic for one reason or another includes the samples of PKS, VWP, ABMC1 + 2 and BCW. The group of candidates with the best overall potential and no apparent critical issues are the BA, OK, OWP, RH and SLU2.

Additional work on the existing samples could be done in order to clarify unanswered questions and reduce uncertainties related to the technical feasibility as well as the overall feasibility of the unproven fuels. This work could include e.g. elemental analysis and ash analysis, defluidization tests, pilot scale proof-of-concept operation, detailed economic feasibility studies and a characterization of the ash fertilizer potential. More complex studies of the existing references with e.g. de-fluidization tests as well as proof-of-concept operation on currently unproven fuels will bring more data to the evaluation criteria of any subsequent screening. It would improve the method significantly if such proof-of-concept operation would be attempted on fuel samples that for one or the other reason look unlikely to succeed (e.g. PKS, VWP, ABM C2 or BCW). This could improve the determination of the severity of various traits and thus improve the method – and potentially decrease the set of experiments required in the analysis.

4. Conclusion

In this work a method for screening new potential fuels for Pyroneer gasification in a Danish setting has been proposed. The method is a simple direct analysis followed by a set of indirect calculations that all together compares a set of fuel characteristics to a set of proven references. The method has been used in a screening process to characterize 18 new potential fuels. Only one fuel is categorized as unsuitable. In addition it was determined that there are 5 of the candidates that look highly problematic, 5 of the candidates that look very promising and 7 candidates that range somewhere in between. Recommendations are given for further improvement of the method and reference database.

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